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An Investigation Conducted by
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Department of Civil Engineering
University of Nevada

EMERGENCY SERVICES TO CONDUCT LABORATORY RESEARCH CONCERNING APPROPRIATE ADDITIONS AT NAS PATUXENT RIVER FUEL FARM IN SITU BIORECLAMATION

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Abstract The effect of total petroleum hydrocarbon (TPH) concentration on the biological treatment of contaminated soils collected from NAS Patuxent River, MD fuel farm was investigated in closed-shake flasks as a basis for future full-scale in situ biological treatment. Soil samples with a TPH concentration of 2,000 mg/Kg were mixed with uncontaminated sand to provide a concentration gradient from 180 to 1,570 mg/Kg TPH. Biological treatment experiments resulted in degradation of hydrocarbons to below detectable levels within 61 days for samples with TPH concentrations of ≤490 mg/Kg. In samples with TPH concentrations of ≥830 mg/Kg, biological treatment resulted in minimal TPH loss over the study period. Specific substrate utilization rates decreased and specific growth rates were not significantly different with increasing TPH concentrations. The data show that microbial growth processes during the logarithmic growth phase were not inhibited at higher TPH concentrations. However, mass transfer limitations and/or toxicity from metabolities formed during logarithmic growth may have caused a decline in microbial numbers resulting in undegraded petroleum residuals in the systems with initial TPH concentrations of ≥830 mg/Kg. In an attempt to increase biological degradation rates, soil samples with an initial TPH concentration of 2,000 mg/Kg were amended with methanol. Treatment with the added methanol resulted in greater TPH degradation over a 34-day period relative to control treatments. Venting of sand and peat soils was investigated to assess the amount of hydrocarbons removed from the vadose zone. Over 83% of the hydrocarbons were removed to 310 mg/Kg TPH from the sandy soil by venting with 270,000 pore volumes of compressed air. Equal amounts of TPH were removed by venting the peat soil, however, air requirements were 294% greater.

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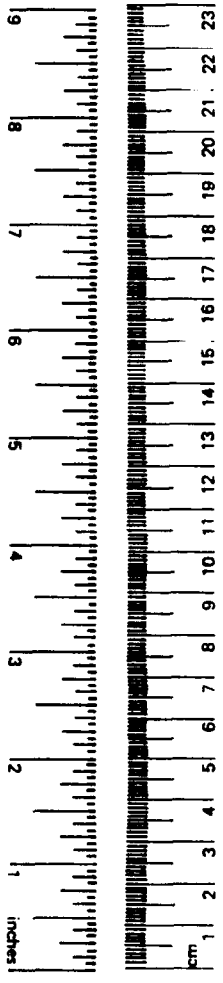
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

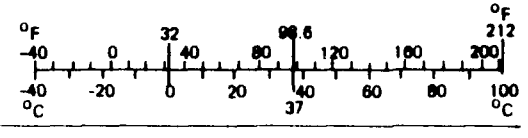
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1,000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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13. ABSTRACT (Maximum 200 words)

The effect of total petroleum hydrocarbon (TPH) concentration on the biological treatment of contaminated soils collected from NAS Patuxent River, MD fuel farm was investigated in closed-shake flasks as a basis for future full-scale in situ biological treatment. Soil samples with a TPH concentration of 2,000 mg/Kg were mixed with uncontaminated sand to provide a concentration gradient from 180 to 1,570 mg/Kg TPH. Biological treatment experiments resulted in degradation of hydrocarbons to below detectable levels within 61 days for samples with TPH concentrations of ≤490 mg/Kg. In samples with TPH concentrations of ≥830 mg/Kg, biological treatment resulted in minimal TPH loss over the study period. Specific substrate utilization rates decreased and specific growth rates were not significantly different with increasing TPH concentrations. The data show that microbial growth processes during the logarithmic growth phase were not inhibited at higher TPH concentrations. However, mass transfer limitations and/or toxicity from metabolities formed during logarithmic growth may have caused a decline in microbial numbers resulting in undegraded petroleum residuals in the systems with initial TPH concentrations of ≥830 mg/Kg. In an attempt to increase biological degradation rates, soil samples with an initial TPH concentration of 2,000 mg/Kg were amended with methanol. Treatment with the added methanol resulted in greater TPH degradation over a 34-day period relative to control treatments. Venting of sand and peat soils was investigated to assess the amount of hydrocarbons removed from the vadose zone. Over 83% of the hydrocarbons were removed to 310 mg/Kg TPH from the sandy soil by venting with 270,000 pore volumes of compressed air. Equal amounts of TPH were removed by venting the peat soil, however, air requirements were 294% greater.

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Introduction

Laboratory studies have been conducted for two years investigating the potential for in situ bioremediation of contaminated soils and groundwater at the Naval Air Station (NAS) Patuxent River fuel farm. The research has been carried out by Battelle Columbus Laboratories, Skidaway Oceanographic Institute, Groundwater Technology, Inc., and the University of Nevada, Reno. In addition, field site assessment has been provided by IT Corporation and Eureka Detection Services. The data obtained during site assessment, laboratory research, and field pilot studies will be used to design in situ soil and groundwater treatment processes.

The contamination at the fuel farm consists of a complex mixture of aromatics, alkyl aromatics, straight-chain aliphatics, and branched-chain aliphatics. Total petroleum hydrocarbon (TPH) concentrations to 20,000 mg/Kg soil have been documented at the site.

The in situ biological treatment of soils and groundwater is based on the addition of nutrients and oxygen to the contaminated system. Nutrient addition stimulates the endemic microbial population resulting in increased biomass with a corresponding ability to metabolize xenobiotics. The microbial transformation of hydrocarbons involves the incorporation of oxygen into the molecule by the use of the oxygenase enzymes. The metabolic process converts the substrate into alcohol, aldehyde, and carboxylic acid intermediates (Alexander, 1977). Once a carboxylic acid is formed, the substrate can enter beta oxidation, which results in the loss of two of the carbons as acetyl-CoA, which is then used for energy and microbial synthesis.

Factors that control the in situ biological treatment of soils and groundwater include the concentration and availability of a terminal electron acceptor, mass transfer, nutrient availability, the biorefractory properties of contaminants, and contaminant toxicity. Oxygen is the most

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common terminal electron acceptor; it is supplied by the injection of compressed air, pure oxygen, or stabilized hydrogen peroxide.

Factors related to the refractory properties of contaminants and their susceptibility to heterotrophic degradation include molecular structure (McKenna, 1977; Atlas, 1984) and microbial species and density (Brock, 1970; Wiggins et al., 1987; Novak et al., 1984; Heitkamp, 1987). Nonbiological factors that affect hydrocarbon degradation are temperature and pH (Alexander, 1977), water solubility (Wodzinski et al., 1972; Alexander, 1985; Thomas et al., 1986), soil adsorption (Alexander, 1985; McCarty et al., 1984), and enzymatic inhibition by soil material (Alexander, 1973).

Contaminants and their metabolites may exhibit microbial toxicity and, therefore, prevent or inhibit growth of heterotrophic organisms (Wiggins et al., 1987). For example, Alexander (1979) stated that hydrocarbon metabolites can be more toxic to microorganisms than the parent compound. Stumm-Zollinger (1968) concluded that a substrate or its metabolites may inhibit microbial anabolic processes.

In its most general sense, toxicity can be defined as the imparting of a deleterious effect, whether lethal or sublethal, to an organism, population, or community. The toxic effect can result in a permanent perturbation such as the destruction of the microbial community. However, not all effects are disruptive, and there exist adaptive mechanisms, both at the cellular level (e.g., detoxifying enzyme systems) and at the population and community levels (Capuzzo, 1981).

Toxic effects from petroleum exposure vary widely and for reasons that are not well understood. The effects are complicated by the varying chemical composition of petroleum products, in which even the same product (e.g., No. 2 fuel oil) refined at a separate location can differ markedly. Laboratory studies have shown that individual aromatic hydrocarbons, unrefined

petroleum, and fractions of petroleum induce a variety of cellular and subcellular alterations in bacteria and invertebrates (Malins, 1982). Sublethal concentrations of oil can change the motile behavior of unicellular organisms or alter metabolic processes that are closely allied with motility. Several metabolic consequences have been suggested including inhibition of bacterial-mediated nutrient regeneration and pollutant removal, disruption of intermicrobial predation, and prevention of phenomena mediated by the settling of mobile microbes on surfaces (Mitchell and Chet, 1975).

Bacteria are repelled by several known components of petroleum including benzene, aniline, and phenol; thresholds for detection average 10^{-4} M (Young and Mitchell, 1973; Tso and Adler, 1974). Most repellents are cytotoxic at concentrations well above those which produce negative chemotaxis. Bacteria detect chemical stimuli by specific protein chemoreceptors, some of which double as active transport enzymes for the substrates with which they combine. The resulting signal is transduced to the flagella via separate membrane-bound chemotaxis proteins (MacNab, 1978). There is circumstantial evidence for the existence of highly specific membrane-bound chemoreceptors in algal gametes as well. Chemotaxis can be inhibited by blocking chemoreception, signal transduction, or the normal functioning of flagella. These processes depend on the normal functioning of the cell membrane which, therefore, provides an accessible target for the action of various petroleum hydrocarbons.

Positive chemotaxis functions to maintain bacterial cells in a nutritionally favorable environment (Bell and Mitchell, 1972). Negative responses serve to remove cells from potentially toxic conditions. Prevention of normal chemotactic behavior can inhibit this important contribution to the general homeostatic mechanism of the bacterial cell and adversely affect microbial activity.

Exposure to petroleum may result in an initial reduction, or even inhibition, of many aspects of native microbial activity including chemotaxis (Bartha and Atlas, 1977). However, oil pollution creates a new set of selective environmental conditions which quickly results in the

development of a hydrocarbon-based microbial community (Barsdate et al., 1980). This may bring with it the development of certain resistances to the otherwise toxic effects of the hydrocarbons as, for example, the carriage of plasmids with the ability to metabolize components of oil (Hada and Sizemore, 1981). Bacteria isolated in the presence of petroleum hydrocarbons have been found to exhibit normal chemotactic responses in the presence of these compounds suggesting an underlying cellular resistance to their effects (Britton et al., 1979). These bacteria may be more representative of the microbial populations which develop after environmental releases of petroleum.

The first year of research investigating the optimum treatment conditions for the NAS Patuxent River fuel farm showed negligible hydrocarbon degradation over 60 days with an initial TPH concentration of 10,000 mg/Kg. In an attempt to explain the low biodegradation rates and to optimize treatment of the site, the second year of research investigated the effect of TPH concentration on the biodegradation rate of weathered petroleum in the NAS Patuxent River fuel farm soil. This study was performed as part of the assessment of JP-5 contaminated soil from the site to provide laboratory data to support field in situ bioremediation.

Methodology

Effect of petroleum concentration on biodegradation rates. Soil collected from the NAS Patuxent River fuel farm was passed through a No. 4 (475mm) sieve to remove rocks and to obtain a homogeneous sample. To investigate the effect of concentration, the contaminated soil was mixed with uncontaminated silica sand to provide soil concentrations of 180, 490, 830, and 1,570 mg/Kg TPH dry weight soil. Fifteen grams of soil were placed in 40 ml borosilicate vials. The vials were then closed (teflon septa caps) and 5 ml of nutrient solution (Restore 375) containing 200 mg/l stabilized H_2O_2 (IT Corporation) were added to provide excess nitrogen and phosphorus (400 mg/l NH_3-N and 20 mg/l PO_4-P). The concentration of oxygen in the head

space was monitored using a Gow-Mac 550 gas chromatograph with a thermal conductivity detector. The oxygen concentration in the head space was correlated with the dissolved oxygen concentration of the soil-water. Parameters included injection port temperature, 60°C; detector temperature, 60°C; column temperature, 60°C; and helium carrier gas flow rate 65 ml/min. Soil-water dissolved oxygen concentrations were maintained at greater than 3 mg/l by the addition of H_2O_2 to the systems through the teflon septa when necesssary. The vials were incubated on an orbital shaker (Lab Line) at 200 rpm; the temperature was maintained at 20°C.

Separate vials were analyzed at ten time intervals over 120 days. The soil slurries were extracted with methylene chloride. The extract was analyzed using an HP 5890A gas chromatograph with a flame ionization detector. A 15 m SPB-1 (Supelco) 0.53 mm capillary column was used with an initial oven temperature of 40°C, final oven temperature of 190°C, and program rate of 7°/min. The injector temperature and detector temperature were 200°C and 220°C, respectively. The nitrogen gas carrier flow rate was 10 ml/min. Other analyses included soil-water dissolved oxygen, pH, NH_3-N, NO_3-N, NO_2-N, and PO_4-P (APHA, 1985). Heterotrophic bacterial counts were determined by serial dilution and plate counts.(APHA, 1985). The plates were incubated at 37°C for 36 hours.

Soil venting. Contaminated cuttings from Well 25 were placed in glass columns 22 cm high and 6.2 cm in diameter. One hundred g of soil were placed in the column resulting in a soil plug 10.2 cm high and 6.2 cm in diameter. Purified compressed air (600 ml/min) was passed through the soil column. Soil venting was carried out for two weeks, with soil aliquots collected every three days and analyzed for total petroleum hydrocarbon concentration and soil moisture content.

Results and Discussion

Bacterial counts and total petroleum hydrocarbon (TPH) concentrations over the 120-day experimental period for the four initial soil TPH concentrations are shown in Figures 1 through 4. Incubation of samples with initial soil TPH concentrations of 180 and 490 mg/Kg resulted in hydrocarbon loss to undetectable levels in 48 and 63 days, respectively. Bacterial counts climbed from 10^5 CFU/g to 10^7 CFU/g over 21 days; the counts then declined to initial numbers.

Samples with initial TPH concentrations of 830 and 1,570 mg/Kg showed 0 and 18 percent TPH degradation over 120 days, respectively. Bacterial counts exhibited a logarithmic growth phase occurring after a lag period. Bacterial numbers increased from 10^5 to approximately 10^7 CFU/g soil. The systems then entered a stationary growth period for 14 days followed by a decrease in bacterial numbers to initial levels.

To evaluate the effect of the initial TPH concentration on soil treatment, specific growth rates (Eq. 1) and specific substrate utilization rates (Eq. 2) were calculated for the logarithmic growth phase in each system:

$$dX/dt = \mu X \quad (1)$$

$$-(dS/dt)/X = kS \quad (2)$$

where

dX/dt	=	microbial growth rate, CFU/g·d
μ	=	specific growth rate, day^{-1}
X	=	bacterial counts, CFU/g
$-(dS/dt)/X$	=	specific substrate utilization rate, (mg/d)/(CFU/g)
k	=	first order rate constant, day^{-1}
S	=	substrate concentration, mg/Kg

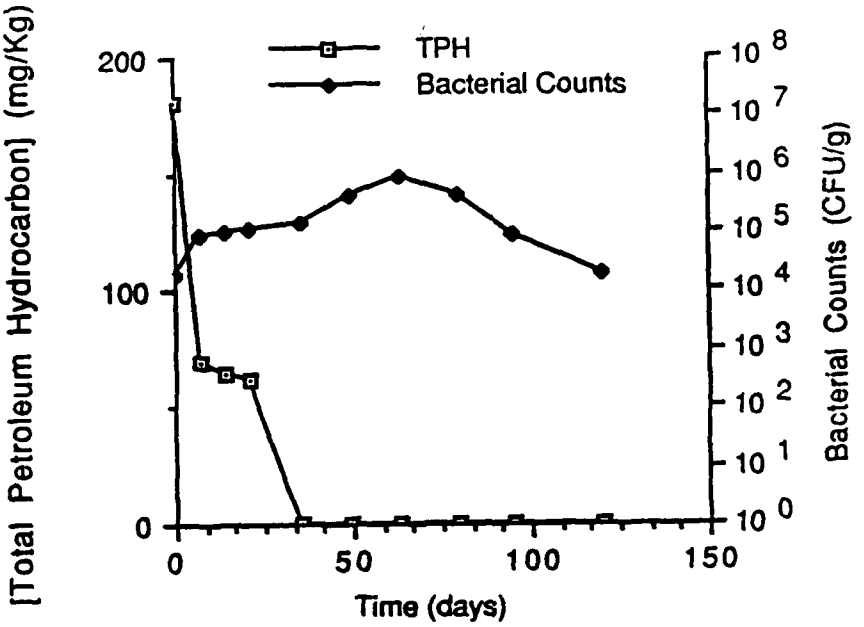

Figure 1. Hydrocarbon biodegradation and bacterial counts with initial TPH concentration of 180 mg/Kg.

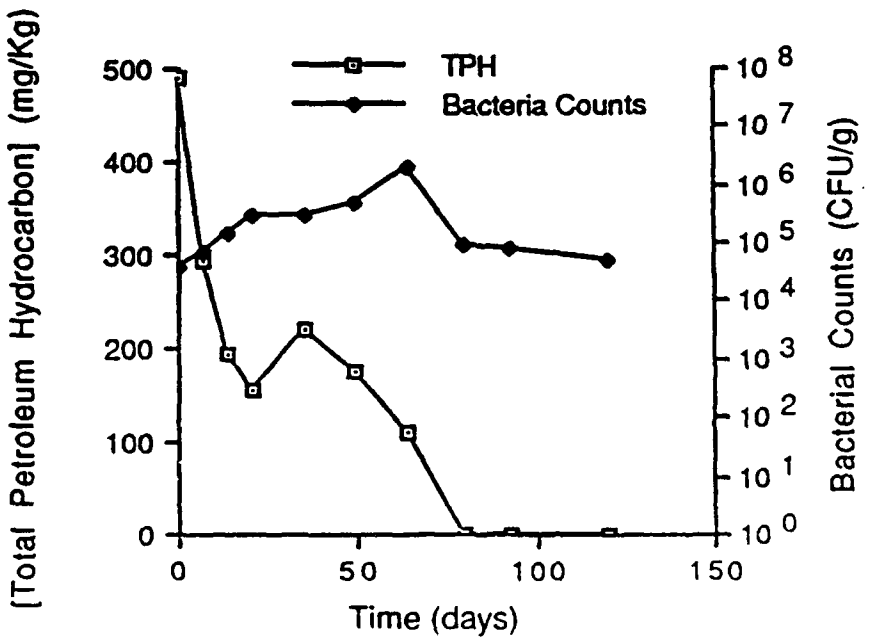

Figure 2. Hydrocarbon biodegradation and bacterial counts with initial TPH concentration of 490 mg/Kg.

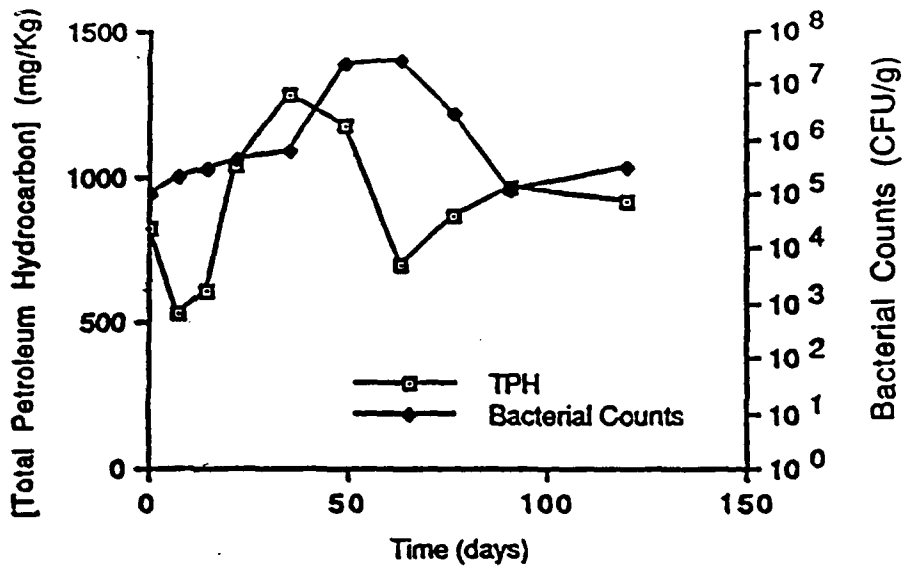

Figure 3. Hydrocarbon biodegradation and bacterial counts with initial TPH concentration of 830 mg/Kg.

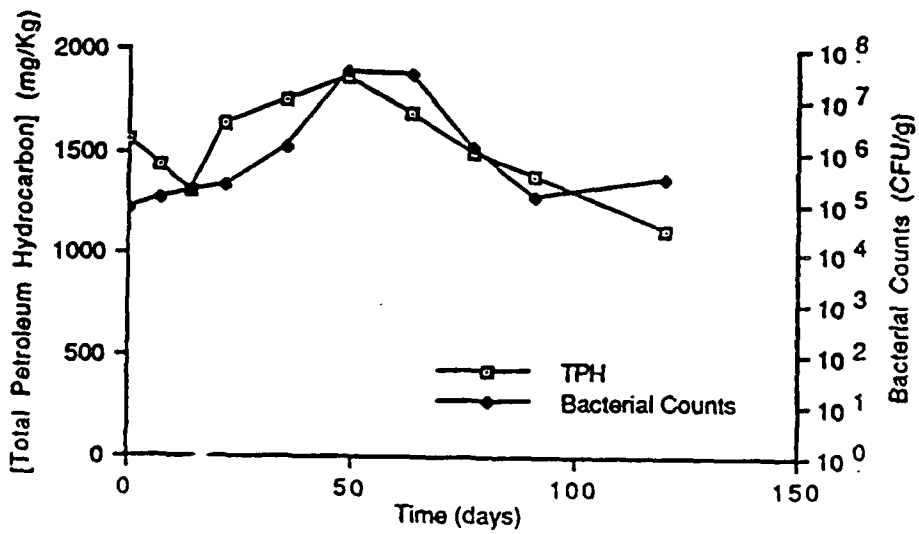

Figure 4. Hydrocarbon biodegradation and bacterial counts with initial TPH concentration of 1,570 mg/Kg.

Equation 2 is applied only to continuous flow stirred tank reactors (CFSTRs) in which steady state substrate and biomass concentrations are established. In batch systems, the specific substrate utilization rate may be approximated by normalizing k to the biomass concentration. Because biomass increased during the batch experiments, k was normalized using the mean X during the logarithmic growth phase. Estimated specific substrate utilization rates are therefore reported as k/X (day^{-1}/CFU/g).

Specific growth rates and estimated specific substrate utilization rates for the four initial TPH concentrations are listed in Table 1. Factorial design analysis of variance (ANOVA) showed that the population means for the four specific growth rates were not significantly different ($\alpha \leq 0.05$). However, ANOVA analysis showed that the estimated specific substrate utilization rates declined as a function of inital TPH concentration ($\alpha \leq 0.05$).

Table 1. Logarithmic phase specific growth rates and estimated specific substrate utilization rates for four initial TPH concentrations.

TPH Concentration (mg/Kg)	Specific Growth Rate $(day)^{-1}$	Specific Substrate Utilization Rate (day^{-1}/CFU/g)
180	0.047	1.03×10^{-6}
490	0.052	5.4×10^{-7}
830	0.093	0
1570	0.111	0

The mechanism of the concentration effect exhibited at TPH concentrations $\geq$ 830 mg/Kg is difficult to elucidate in such a complex system. Growth and heterotrophic metabolism were not limited by dissolved oxygen, pH, or nutrients. The dissolved oxygen concentration in the systems

was maintained at $\geq$ 3 mg/l and the pH did not decrease below 6 (Figure 5). The concentrations of the two primary nutrient additions, NH_3-N and PO_4-P, decreased negligibily during the 120-day treatment (Figures 6 and 7). Difficulties in treating hydrocarbons have often been attributed to the biorefractory nature of some petroleum fraction (e.g., branched alkanes) (Wilson and Ward, 1987). However, a biorefractory residual did not remain after 48 and 61 days in the systems with 180 and 490 mg/Kg initial TPH concentrations, respectively. The decline in biomass with a corresponding halt to biodegradation in the 830 and 1,570 mg/Kg TPH systems cannot be attributed to a biorefractory fraction of the hydrocarbons, because a residual would have also remained in the lower TPH systems. Therefore, the hydrocarbons in the soil at the NAS Patuxent River fuel farm were not biorefractory under the conditions of the laboratory treatment.

The low degradation rates characteristic of the high TPH concentrations may be due to a surface area phenomenon. Bacteria may not be physically capable of degrading hydrocarbons when, at high concentrations, the substrate is present in water insoluble films and globules. (Stucki and Alexander, 1987; Thomas et al., 1986).

The increase in biomass shown in Figures 3 and 4 must be attributed to the anabolism of a carbon source. Microbial growth could result from the metabolism of naturally occurring soil organic carbon or biologically available petroleum. Metabolism of petroleum is not apparent from Figures 3 and 4, because an increase in biomass must correspond to a decrease in the TPH concentration. However, the biodegradation of hydrocarbons may be masked by common analytical procedures. Brown (1989) postulated that the increased number of microorganisms in soil treatment systems releases biosurfactants which may increase the hydrocarbon extraction efficiency. Such an increase in extraction efficiency in the shake flasks used in this research may have masked TPH biodegradation over the first 49 days of treatment. Based on Brown's hypothesis, postulated TPH concentrations are shown in Figures 8 and 9 for the 830 and 1,570 mg/Kg initial measured TPH concentrations, respectively. Regardless of the carbon source for

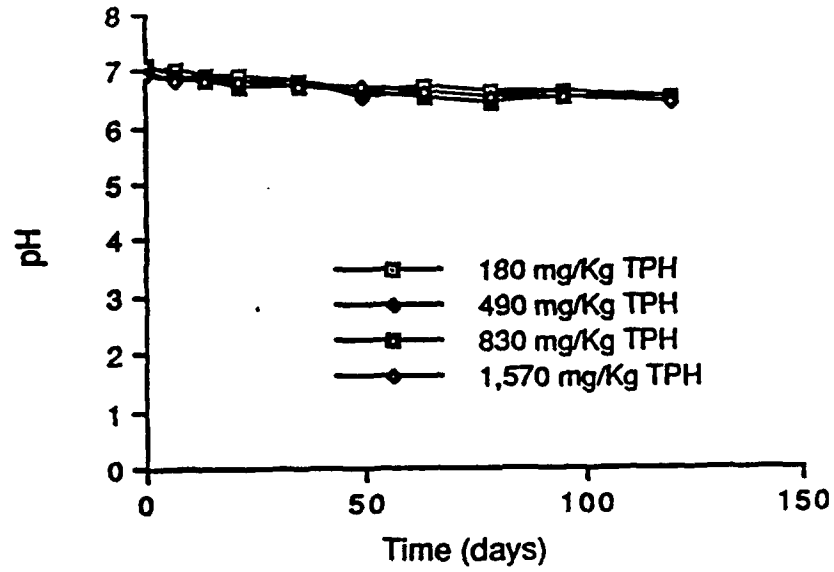

Figure 5. pH levels during biodegradation studies.

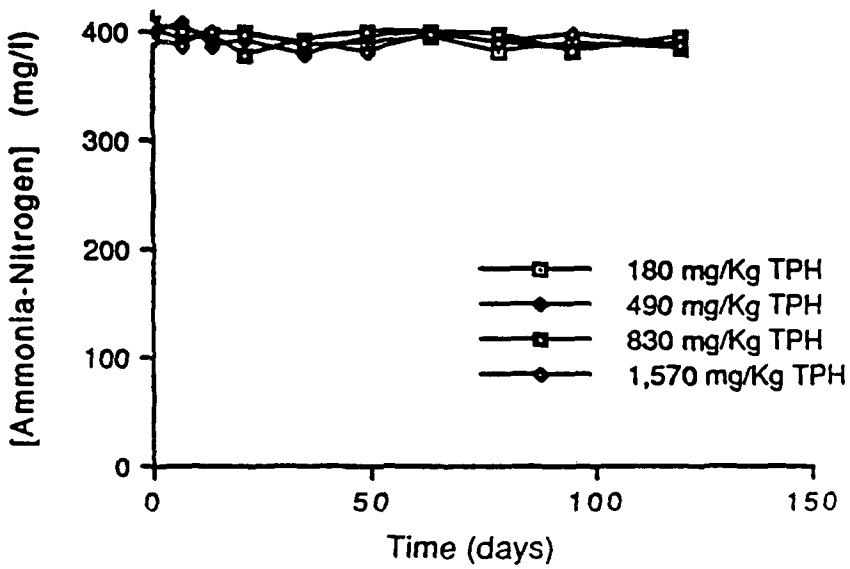

Figure 6. Ammonia-nitrogen concentrations during biodegradation experiments

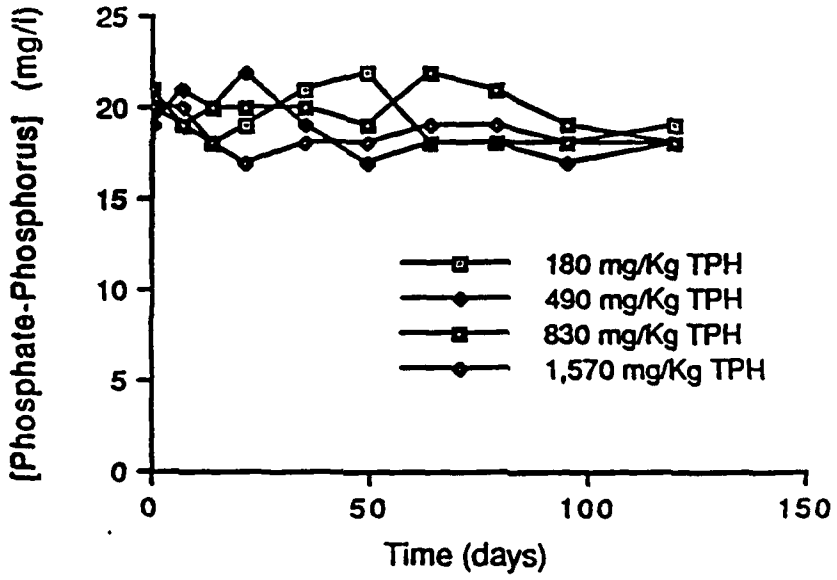

Figure 7. Phosphate-phosphorus concentrations during biodegradation experiments.

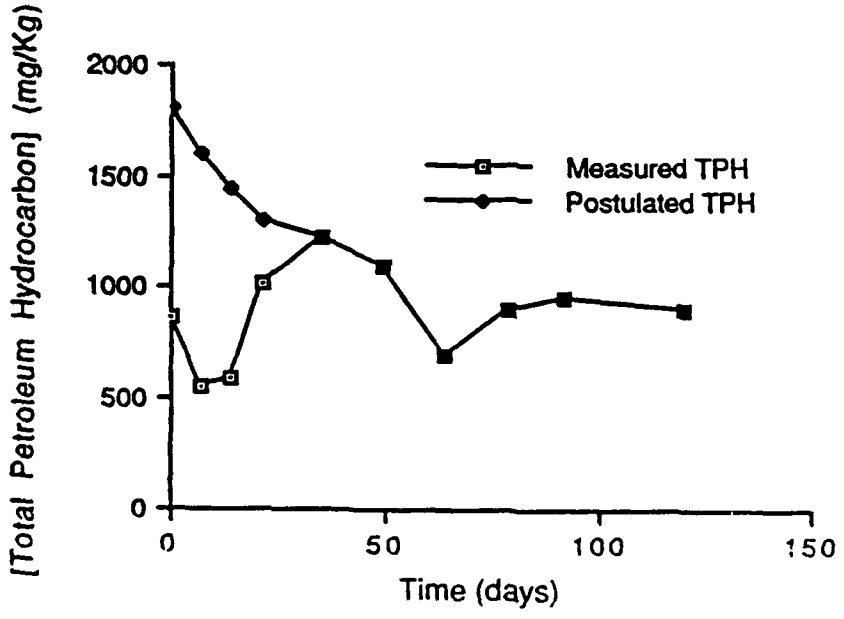

Figure 8. Hydrocarbon biodegradation using the postulated initial TPH concentration in the system with initial measured TPH concentration of 830 mg/Kg.

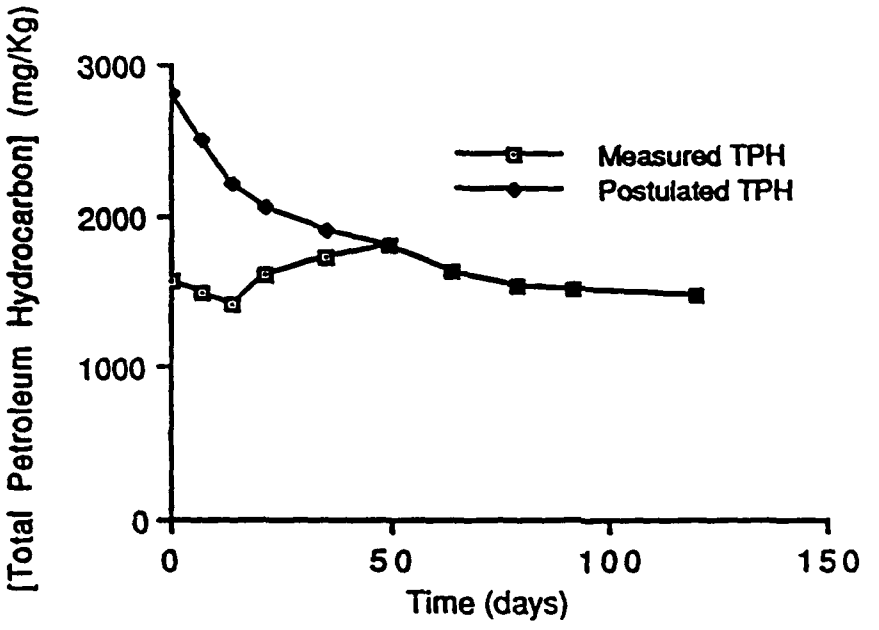

Figure 9. Hydrocarbon biodegradation using the postulated initial TPH concentration in the system with initial measured TPH concentration of 1,570 mg/Kg.

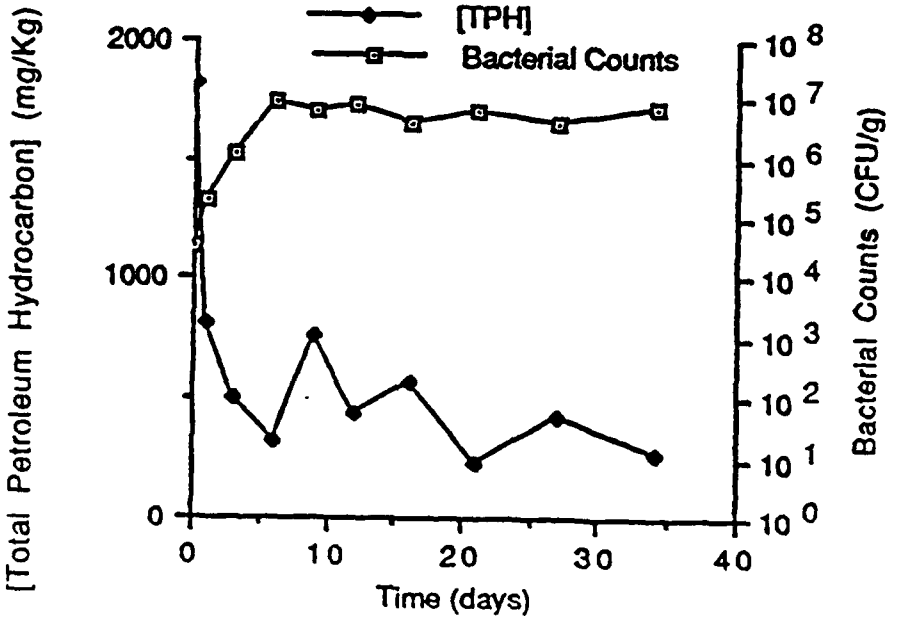

Figure 10. Biodegradation and bacterial counts during treatment with methanol ammendment.

microbial growth in the two high TPH systems, microbial counts began to decline to original levels after 63 days leaving the final TPH residual at approximately 830 mg/Kg (for the 830 mg/Kg initial concentration) and 1,260 mg/Kg (for the 1,570 mg/Kg initial concentration). If Brown's hypothesis is correct, the most likely explanation of the laboratory treatment data is the production of toxic metabolites as exponential growth proceeded. The toxicity would have then resulted in a decline in bacterial counts and a halt to hydrocarbon degradation (Alexander, 1979).

Inhibition of metabolic processes due to high contaminant concentration has been documented in other bioremediation studies. Hickman and Novak (1984) reported enzymatic inhibition in the biological degradation of pentachlorophenol. Mitchell and Chet (1975) suggested that microbial chemosensory attrition was inhibited by crude oil. Novak et al. (1985) reported that methanol was biodegradable up to 1,000 mg/l, while tertiary butyl alcohol was not degraded at concentrations greater than 100 mg/l. These studies lend support to possible toxicity of metabolites produced during the first 49 days of treatment. Therefore, the most likely mechanisms causing the concentration effect at high TPH concentrations were mass transfer limitations and/or toxicity and subsequent metabolic inhibition of the hydrocarbon metabolites.

One difference between the results of this research and the results obtained in other laboratory petroleum treatment studies is the reaction vessel used. This study used a closed, batch system in which volatilization and dilution did not to occur. Many other petroleum biodegradability studies have used systems open to the atmosphere (Jamison et al., 1975). Volatilization is difficult to control in open systems; therefore, biodegradation rates may be overestimated in systems open to the atmosphere. Continuous flow systems have also been used for laboratory biodegradability studies (Vanloocke et al., 1975). The closed batch system used in this study provides a more conservative estimate of field biodegradability because toxic metabolites would not be removed as in a flow-through system.

To evaluate the potential of stimulating the biodegradation of petroleum with TPH concentrations greater than 830 mg/Kg, the treatment experiments were repeated with a methanol ammendment. Well cuttings (Well 23) containing 2,000 mg/Kg TPH were prepared in the same manner as in the first experiment, but methanol was added to a final concentration of 10 mg/l in the soil-water solution. Due to the high methanol biodegradation rate, 10 mg/l of methanol were also introduced once per week over the 34-day treatment period. The pH was maintained above 6.0 by the addition of 1 M NaOH when necessary.

Figure 10 shows the results of the treatment with methanol amendment. Microbial growth immediately entered a logarithmic growth phase for 6 days then remained in a stationary phase for the remainder of the experiment. Figure 10 shows that the methanol ammendment resulted in an 83% loss of TPH over the 34-day experimental period.

The specific growth rate and estimated specific substrate utilization rate for the methanol - amended system were 0.87 day^{-1} and 2.28 x 10^{-5} day^{-1}/(CFU/g), respectively. By factorial ANOVA, these values are significantly greater than the specific growth rates and estimated specific substrate utilization rates for the 830 mg/Kg and 1,570 mg/Kg TPH experiments. In addition, bacterial counts were maintained at 10^7 CFU/g, which provided sufficient biomass for continued metabolism throughout the 34-day experiment. The sustained growth in the methanol-ammended system suggests that the toxicity of metabolites may not be the predominant mechanism for the concentration effect at TPH concentrations $\geq$ 830 mg/Kg. The increased growth rates and substrate utilization rates may be due to increased solubility of hydrocarbons (i.e. a surfactant effect). Alternatively, a cometabolic or other biochemical mechanism associated with methanol addition may have provided the necessary metabolic potential to enhance hydrocarbon treatment. McCarty (1985) proposed the addition of an alternative carbon source to enhance the treatment of some contaminants, particularly at low concentrations. The addition of methanol may, therefore,

offer potential for increasing biodegradation rates in the soil and groundwater at the NAS Patuxent River fuel farm.

When considering in situ bioreclamation, the primary factors are cost and liability. Nyer (1985) estimated that in situ biological treatment provides a five-fold cost savings and substantially reduces future liabilities relative to excavation, removal, and disposal. In situ bioremediation, combined with other treatment processes, has been successful in reducing organic contaminants in groundwater (Lee et al., 1989). However, Healy and Daughton (1986), in reviewing the bioremediation literature, argued that the positive results seen with in situ treatment may be attributed to sampling errors, dilution, and physicochemical processes. Based on the results of this research, high TPH concentrations may also be a factor that significantly influences the efficacy of in situ bioremediation.

Soil venting. Compressed air flow rates and soil temperatures during the course of the soil venting experiments for the sandy soil and the peat soil collected from surface seeps at the NAS Patuxent River fuel farm are shown in Figures 11 and 12, respectively. These data show that the air flow rate was relatively constant at approximately 0.60 l/min and that the temperature was uniform at 25°C. Total petroleum hydrocarbon concentrations as a function of the volume of air purged through the sand system are shown in Figure 13. These data show that greater than 83% of the TPH were removed from the sandy soil to 310 mg/Kg TPH with 9,000 L of air. During the venting process, approximately 1,500 mg/Kg of TPH were volatilized. Assuming a bulk density of 1.2 g/cm^3 and porosity of 0.4 for the soil, the venting requirement for the sandy soil is 270,000 pore volumes. Residual TPH concentration and moisture during venting of the peat soil are shown in Figure 14. These data show that the same percentage of hydrocarbons can be stripped from the peat soil as the sandy soil, but air volume requirements were 294% greater at 26,500 L of air.

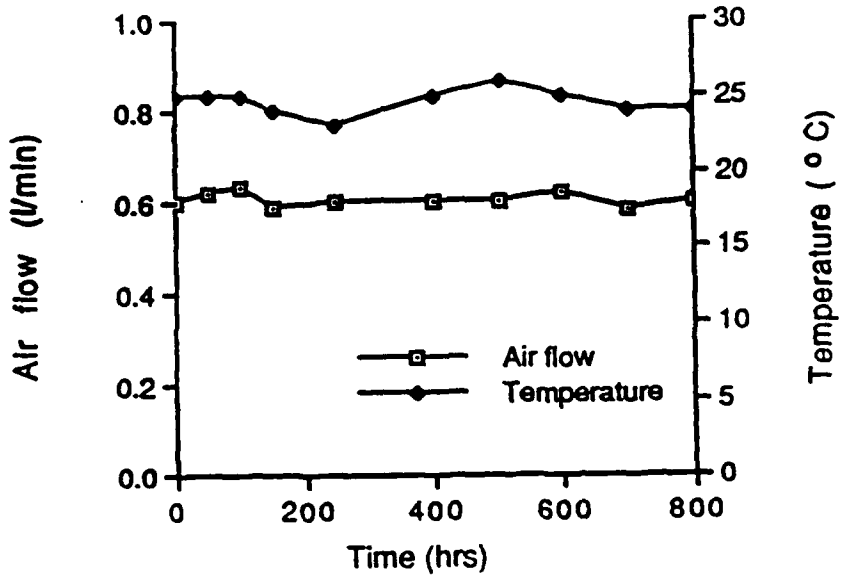

Figure 11. Air flow rates and temperature during soil venting of the sandy soil.

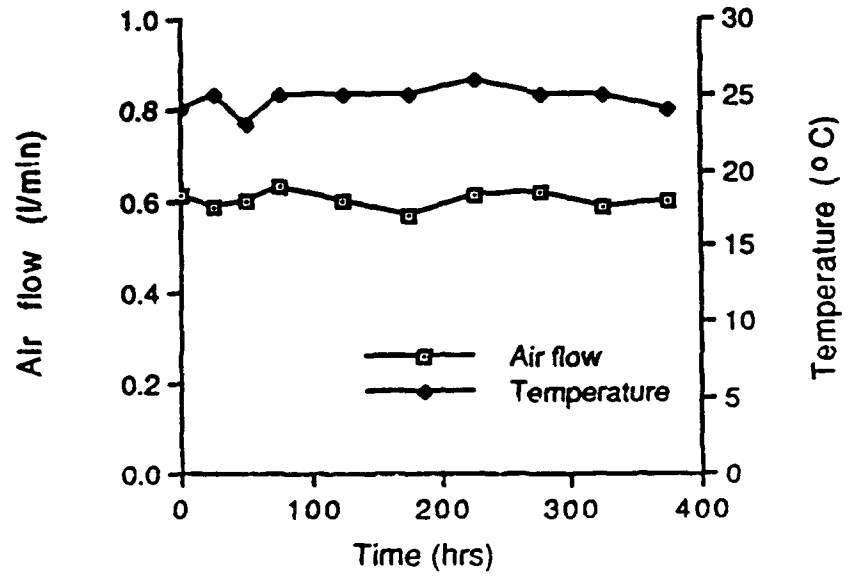

Figure 12. Air flow rates and temperature during soil venting of the peat soil.

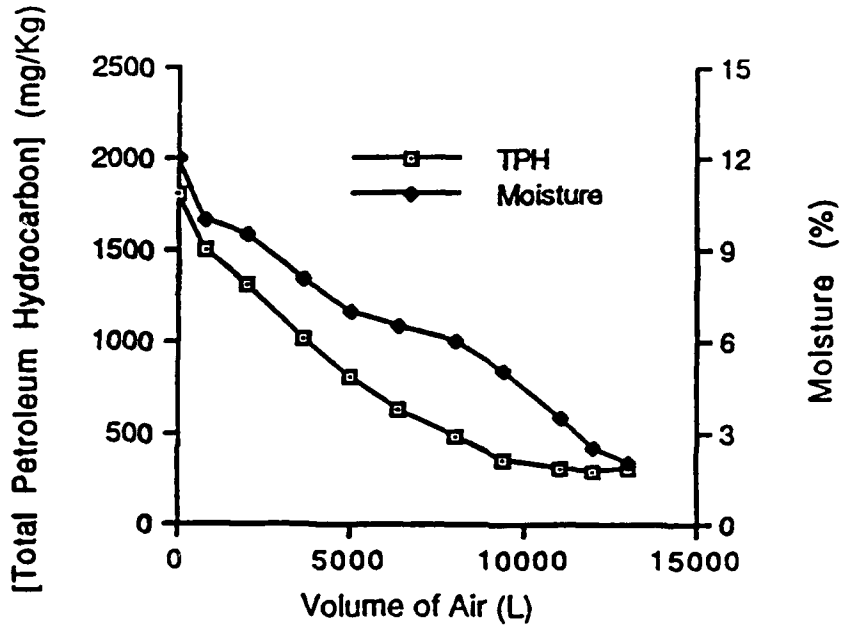

Figure 13. Total petroleum hydrocarbon concentrations and soil moisture content during venting of the sandy soil.

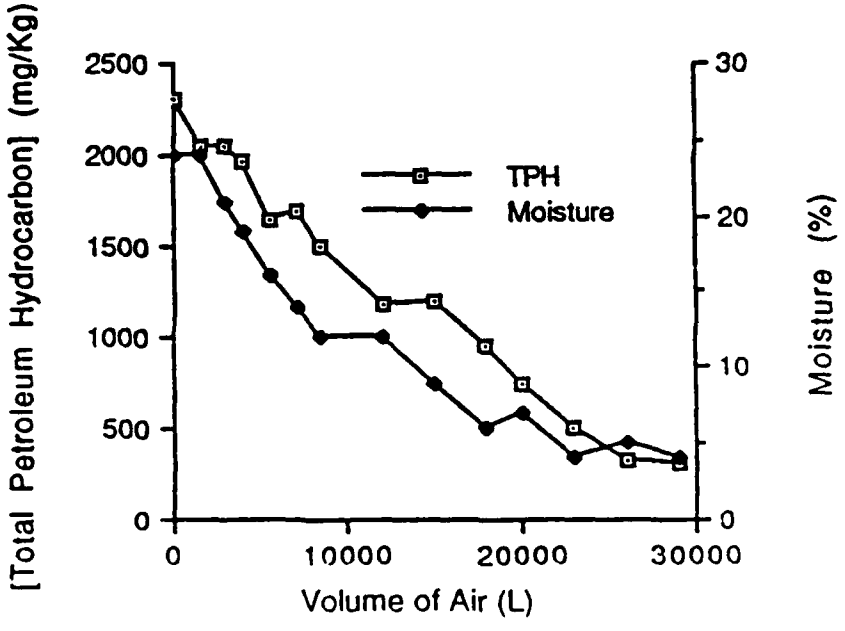

Figure 14. Total petroleum hydrocarbon concentrations and soil moisture content during venting of the peat soil.

Summary and Conclusions

Closed-system shake flask treatability experiments were conducted on NAS Patuxent River soils contaminated with weathered products resulting from JP-5 jet fuel releases. The flasks received nitrogen, phosphorus, and stabilized hydrogen peroxide additions and were incubated for 120 days at 20°C. Total petroleum hydrocarbon, nitrogen and phosphorus species, dissolved oxygen, and peroxide concentrations, and pH were determined at ten times over the 120 days. Soil venting was also investigated as a means of removing high TPH concentrations prior to bioremediation. Two soils (sandy, organic) were purged with compressed air for two weeks. Total petroleum hydrocarbon concentration, temperature, and moisture content were monitored over the time of study. The following conclusions may be drawn from the study:

1. Estimated logarithmic phase specific substrate utilization rates for hydrocarbon biodegradation decreased as a function of initial TPH concentration. Specific growth rates were unaffected by initial TPH concentration.

2. Petroleum hydrocarbons in the NAS Patuxent River fuel farm were not biorefractory under the laboratory treatment conditions.

3. The concentration effect during hydrocarbon treatment was attributed to mass transfer limitations and/or toxicity of metabolites produced during the first 49 days of treatment.

4. The results of the treatment methodology developed through this research provide a more conservative approach to hydrocarbon treatability compared to other methodologies because volatilization, dispersion, and dilution are minimized.

5. Methanol amendment enhanced estimated specific substrate utilization rates and specific growth rates. Methanol additions maintained plate counts in a stationary phase; solubilization of the hydrocarbons may have also enhanced biodegradation.

6. Greater than 83% of the TPH were removed from the sandy soil with 9,000 L of air. The same percentage of hydrocarbons were stripped from the peat soil, but air requirements were 294% greater.

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